

# Electronic Structure, Phase Stability and Resistivity of Hybrid Hexagonal $C_x(BN)_{1-x}$ Two-dimensional Nanomaterial: A First-principles Study

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## Abstract

We use density functional theory based first-principles method to investigate the bandstructure and phase stability in the laterally grown hexagonal  $C_x(BN)_{1-x}$ , two-dimensional Graphene and  $h$ -BN hybrid nanomaterials, which were synthesized by experimental groups recently (Liu *et al*, Nature Nanotech, **8**, 119 (2013)). Our detail electronic structure calculations on such materials, with both armchair and zigzag interfaces between the Graphene and  $h$ -BN domains, indicate that the band-gap decreases non-monotonically with the concentration of Carbon. The calculated bandstructure shows the onset of Dirac cone like features near the band-gap at high Carbon concentration ( $x \sim 0.8$ ). From the calculated energy of formation, the phase stability of  $C_x(BN)_{1-x}$  was studied using a regular solution model and the system was found to be in the ordered phase below a few thousand Kelvin. Furthermore, using the Boltzmann transport theory we calculate the electrical resistivity from the bandstructure of  $C_x(BN)_{1-x}$  at different temperature ( $T$ ), which shows a linear behaviour when plotted in the logarithmic scale against  $T^{-1}$ , as observed experimentally..

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## Introduction

Ever since the discovery of Graphene by Geim, Novoselov and co-workers [1, 2], a great deal of effort has been put to make Graphene functionalized by engineering a controllable band-gap between its valence and conduction bands. Hexagonal Boron Nitride ( $h$ -BN), having lattice constant very close to that of Graphene and an insulating band-gap of nearly 5-eV, which can be easily synthesized in the form of

monolayer flakes [3, 4], provides a wide range of possibilities to mix with Graphene to yield a varying band-gap material depending on the degree of mixing [5]. As such materials are of great importance in optoelectronic devices, a great deal of effort has been made to synthesize hexagonal CBN ( $h$ -CBN) monolayer and multilayer nanomaterials [6, 7, 8, 9] with varying concentration of C / BN.

Experimentally  $h$ -CBN was synthesized initially

by Panchakarla et al [6] and by Ci et al [7] using Chemical Vapour Deposition (CVD) technique, where concentration of C or BN was carefully controlled. All *h*-CBN samples were reported to exhibit semiconducting behavior showing a band-gap varying between a few meV to nearly an eV, a fact which has been verified by first-principles calculations [10]. Formation of a band-gap in Graphene, when doped by Boron and Nitrogen, has been studied earlier [11, 12, 13, 14, 15, 16]. It was shown that upon Boron (hole) doping the Dirac cone in Graphene is moved above the Fermi level and a gap appears, whereas upon Nitrogen (electron) doping the Dirac cone is moved below the Fermi level [17]. Upon co-doping of Graphene by both B and N a gap appears between the conduction and valence bands making *h*-CBN a semiconductor where the band gap depends sensitively on the degree of doping and also on the thickness of the layer.

Very recently, Liu et al [18] have reported on synthesis of in-plane laterally grown heterostructures of Graphene and *h*-BN where these two materials are seamlessly integrated lithographically with varying domain sizes. This astounding synthesis of laterally grown hybrid  $C_x(BN)_{1-x}$  two-dimensional heterostructure, with domain shapes such as circular dots, stripes and patterns etc of varying sizes and width, has made the possibility of device application of such materials a reality. Similar synthesis of hybrid *h*-CBN have been recently carried out by other groups [19, 20, 21] using different experimental con-

ditions.

Several calculations have been reported on the electronic structure [11, 12, 13, 14, 15, 16, 22, 23] and also on the stability of  $C_x(BN)_{1-x}$  [24]. In this paper we calculate the phase stability of CBN from the free energy using a regular solution model and apply the transport theory of band electrons on our DFT bandstructure to obtain the temperature dependent resistivity at different concentration of  $C_x(BN)_{1-x}$ , which were not been addressed before.

Since, the interface between such domains can be either armchair or zigzag type, we have studied both the interfaces using a large  $5 \times 5$  unit cell. Recently, few such calculations [25, 26] have been reported, but these authors have defined different unit cell types for armchair and zigzag interfaces. In the present calculation the unit cells for both armchair and zigzag interfaces are consistently similar giving rise to hexagonal Brillouin zone for each of these interfaces. We have consistently varied the concentration of C (or BN) as 0.2, 0.4, 0.6 and 0.8 and have calculated the band structure, density of states, charge density and formation energy of  $C_x(BN)_{1-x}$ . Our calculated band structure for each of those interfaces show the emergence of Dirac-cone like features with increasing C concentration. *h*-BN has a band gap of nearly 5 eV whereas Graphene has zero band gap at the high symmetric K-point in the hexagonal Brillouin zone, so it is expected for the band gap to decrease with the increasing C concentration, ultimately becoming zero for  $x = 1$ . We obtained a non-monotonic decrease of

the band gap for  $C_x(\text{BN})_{1-x}$  with increasing  $x$  and the concentration dependence of the band gap is different for the armchair and zigzag interfaces. Our calculated DOS and charge density indicate that the charge transfer effects might play important role in the band gap formation. Moreover, from the calculated formation energy, we studied the phase stability of  $C_x(\text{BN})_{1-x}$  using a regular solution model and estimated the order-disorder transition temperature. It was found that the onset of substitutional disorder would occur at temperatures of  $\sim 3850\text{K}$  and  $6090\text{K}$  for the zigzag and armchair interfaces, respectively.

Finally, we use the Boltzmann transport theory applied to the band electrons [27] to calculate the electrical conductivity ( $\sigma$ ) [28] from the bandstructure of  $C_x(\text{BN})_{1-x}$  calculated earlier. From the calculated  $\sigma(T)$  we obtain the resistivity  $\rho(T)$ , which shows a linear behaviour when plotted in the logarithmic scale against  $T^{-1}$ , as expected for semiconductors and as measured experimentally for  $C_x(\text{BN})_{1-x}$  [7, 10].

## Method of Calculation

We carried out the *ab-initio* DFT calculations on the  $5 \times 5$  *h*-CBN unit-cell with armchair and zigzag (Fig. 1) interfaces using the Quantum Espresso code [29]. A hexagonal unit cell was chosen for both the armchair and zigzag case. The plane wave calculations assume periodicity and hence to avoid interactions between the sheets, a vacuum spacing of  $13\text{\AA}$  was chosen. We have used the ultrasoft pseudopo-

tential [30] to describe the core electrons and the generalized gradient approximation (GGA) for the exchange-correlation kernel [31]. A kinetic energy cutoff of  $40\text{Ry}$  was used for the plane-wave basis set and of  $160\text{Ry}$  for the charge density, and an accuracy of  $10^{-9}\text{Ry}$  was obtained in the self-consistent calculation of total energy. The equilibrium lattice constants were obtained by minimizing the total energy with respect to the lattice constants by ensuring that the stress on each of the atoms are zero. The self-consistent calculations were performed using a converged Monkhorst-Pack  $k$ -point grids [32] of  $6 \times 6 \times 1$ . Band structure calculations were performed for the equilibrium lattice constants with 150  $k$ -points along the high-symmetric points  $\Gamma$ -K-M- $\Gamma$  in the irreducible hexagonal Brillouin zone for both armchair and zigzag interfaces.

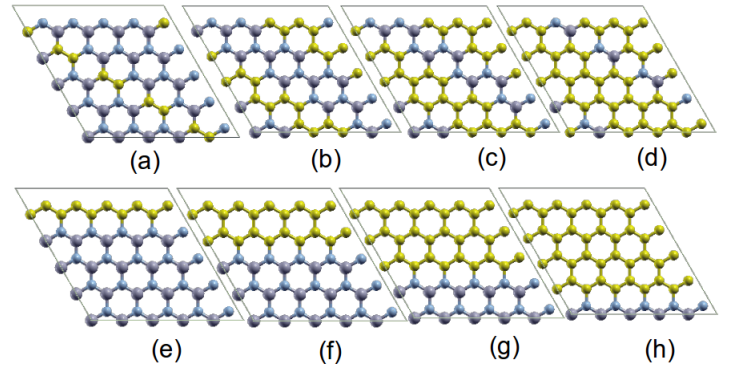


Figure 1:  $5 \times 5$  unit-cell of  $C_x(\text{BN})_{1-x}$  with armchair interface (a, b, c, d) and zigzag interface (e, f, g, h), between Graphene and *h*-BN domains, at  $x = 0.2, 0.4, 0.6$  and  $0.8$ ; respectively. Carbon atoms are denoted by yellow, Boron by grey and Nitrogen by blue colored balls; respectively.

We obtained the in-plane lattice constant  $a_0$  as 2.466 Å and 2.508 Å for Graphene and  $h$ -BN, respectively, which compare well with the experimental values. For  $C_x(BN)_{1-x}$  system the equilibrium lattice constant lies in between that of Graphene and  $h$ -BN and it was calculated for different concentrations for each interface types. The total density of states (DOS) and the partial densities of states (PDOS) projected on each orbital on the in-equivalent atoms in the unit cell were calculated for all concentrations and the Löwdin charge [33] is also obtained. The Xcrysden code [34] was used for visualizing the valence charge densities.

For the calculation of the resistivity  $\rho(T)$  of  $C_x(BN)_{1-x}$  from the calculated bandstructure we use the Boltzmann transport theory for band electrons as implemented in the code BoltzTrap [28]. This calculation involves the evaluation of the electron group velocity  $v_\alpha(i, \mathbf{k})$  referring to  $i$ -th energy band and the  $\alpha$ -th component of the wave vector  $\mathbf{k}$ , from the band dispersion  $\varepsilon(i, \mathbf{k})$ , expressed as,

$$v_\alpha(i, \mathbf{k}) = \frac{1}{\hbar} \frac{\partial \varepsilon(i, \mathbf{k})}{\partial k_\alpha}. \quad (1)$$

The electrical conductivity tensor is then obtained from,

$$\frac{\sigma_{\alpha\beta}(T, \mu)}{\tau} = \frac{1}{V} \int e^2 v_\alpha(i, \mathbf{k}) v_\beta(j, \mathbf{k}) \left[ \frac{-\partial f_\mu(T, \epsilon)}{\partial \epsilon} \right] d\epsilon, \quad (2)$$

where  $\mu$  is the chemical potential,  $f_\mu$  is the Fermi-Dirac distribution function,  $V$  is the volume of the sample, and  $\tau$  is the Drude relaxation time which is assumed to be isotropic and direction independent [35, 36]. The resistivity is then obtained from the conductivity as,  $\rho = 1/\sigma$ . The relaxation time  $\tau$  is typically  $\sim 10^{-14}$ s [27] but a precise value of this quantity

is unknown for  $C_x(BN)_{1-x}$ . For the calculation of the resistivity of  $C_x(BN)_{1-x}$  we have taken a very dense k-point grid of  $40 \times 40 \times 1$  and even denser grid was taken at some concentrations for the band structure calculation using Quantum Espresso code, which was then fed into the BoltzTrap code for the transport calculation.

## Results and Discussion

### (a) Electronic structure

In Fig. 2 we show the bandstructure and the corresponding density of states (DOS) of  $C_x(BN)_{1-x}$  for  $x = 0.2, 0.4, 0.6$  and 0.8, for both armchair and zigzag interfaces between the Graphene and  $h$ -BN domains. The DOS shown in Fig. 2 refers to total DOS (including  $2s$ ,  $2p_x$ ,  $2p_y$  and  $2p_z$  contributions) of Carbon, Boron and Nitrogen atoms in the unit-cell and also the partial density of states (PDOS) of  $2p_z$  orbitals on each of those atoms. The DOS and PDOS were calculated for all nonequivalent atoms in the unit-cell, so that in the figures they appear appropriately weighted. The Fermi energy is at the middle of the energy gap between the conduction and the valence bands. It should be recalled that  $\pi$  and  $\pi^*$  bands of carbon dominate the electronic structure of undoped Graphene around  $E_F$ , and  $\pi^*$  bands of B and  $\pi$  bands of N represent the conduction and valence bands of  $h$ -BN, above and below its energy gap [37], respectively. It is clear from the DOS results shown in Fig. 2 that the nature of the bands around the energy gap of  $C_x(BN)_{1-x}$  are essentially due to  $2p_z$  states of C, B and N, as the total DOS is completely dominated by PDOS of  $2p_z$  state, around 2.5eV each above and below the band gap for all concentrations.

The bandstructure in Fig. 2 shows that the band gap of  $C_x(BN)_{1-x}$  decreases with increasing concentration of C. Since the band gap of undoped  $h$ -BN is calculated to be 4.76-eV, the band gap of  $C_x(BN)_{1-x}$  decreases from this value with increasing C-concentration upon mixing with Graphene until it becomes zero for  $x = 1$ . The nature of the decrease of the band gap with increasing  $x$  was found to be non-monotonic and

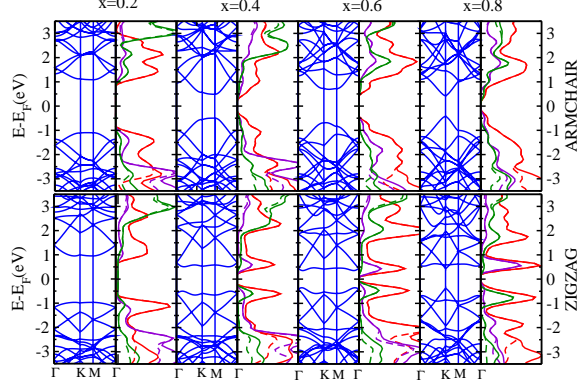


Figure 2: The calculated bandstructure and the density of states (DOS) of  $C_x(\text{BN})_{1-x}$  at  $x = 0.2, 0.4, 0.6$  and  $0.8$  for armchair (upper panel) and zigzag (lower panel) interfaces. The Fermi energy is at the centre of the band gap. The bands (blue) are shown in the high-symmetry directions  $\Gamma$ -K-M- $\Gamma$  in the hexagonal Brillouin zone. The total DOS is shown as full-line for C (red), N (violet) and B (green); the corresponding projected density of states (PDOS) of  $2p_z$  states for each atoms being shown as dashed-line with similar colors, respectively. The DOS and PDOS are in arbitrary units.

different for armchair and zigzag interfaces between Graphene and  $h$ -BN domains as shown in Fig 3., to be discussed later. For the armchair interface the minimum band gap appears near the high symmetric M-point of the hexagonal Brillouin zone for  $x = 0.2$  and  $0.4$ . For  $x = 0.6$ ,  $C_x(\text{BN})_{1-x}$  behaves as an indirect band gap material for the armchair interface, with the minima of the conduction band lying between the high symmetric K- and M-points. This behavior changes at higher C-concentration when at  $x = 0.8$ , Dirac cone-like feature appears at the K-point in both armchair and zigzag interfaces, as expected for Graphene. For the zigzag interface,  $C_x(\text{BN})_{1-x}$  behaves as indirect gap material for  $x = 0.2, 0.4$  and  $0.6$ . At  $x = 0.8$  the direct band gap at K-point is very close to that of armchair case. We would like to emphasize that all our self-consistent calculations were performed by relaxing the lattice, but keeping the hexagonal symmetry, to assure zero strain in

the unit cell. In this way, we have obtained the equilibrium in-plane lattice constant  $a(x)$  for each concentration. We would like to add that our calculations were performed for the spin polarized case. The spin up and spin down components of the DOS happen to be exactly the same unlike reported by [11, 12, 13, 14, 15, 16]. The reason for this is that those calculations are performed on nanoribbons. The spin polarization on each atom diminishes as we move into the nanoribbon [38]. In this paper all our calculations are studied on an infinite sheet and hence there are no spin polarization on any atom.

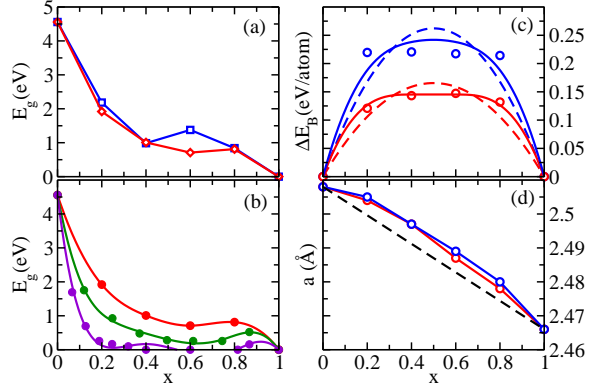


Figure 3: Various calculated physical properties of  $C_x(\text{BN})_{1-x}$  shown as a function of  $x$ , both for armchair (blue) and zigzag (red) interfaces between Graphene and  $h$ -BN domains. (a) The minimum band gap. (b) Band gap for the zigzag interface fitted with Eq (1), shown for present calculation (red), that of  $8 \times 8$  cell (green) and that of  $16 \times 16$  cell (violet) of Bernardi *et al* [25]. (c) Formation energy  $\Delta E_B$  for both type of interfaces. Calculated data are shown as open circles. Parabolic fit by functions  $4\Delta H x(1-x)$  are shown as dashed lines. A fit by a function of the form  $H_0 + H_1 x(1-x) + H_2 x^2(1-x)^2$  are shown by solid lines. (d) The equilibrium in-plane lattice constant  $a$ . The dashed line refers to Vegard's law.

In Fig. 3 the calculated band gap  $E_g$ , the formation energy  $\Delta E_B$ , and the equilibrium lattice constant  $a$  are shown for  $C_x(\text{BN})_{1-x}$  as a function of  $x$ , for the armchair and zigzag

interfaces. The calculated  $E_g$  indicates Fig. 3(a), for both armchair and zigzag interfaces, the indirect band gap to be slightly smaller than the direct band gap at high-symmetric K-point for  $x < 0.8$ . For  $x \geq 0.8$ , the Dirac cone-like features start evolving and the band gap is a direct one at K-point. This non-monotonic behavior of  $E_g$ , which has also been observed in recently published calculations [25, 26], is apparently not observed in the semiconductor alloys. This dependence can be incorporated by taking higher order concentration dependent terms in the optical bowing parameter [39], so we have fitted a fifth-order polynomial to best describe the  $x$  dependence of  $E_g$  for  $C_x(\text{BN})_{1-x}$ , given as,

$$E_g(x) = [E_g^{h\text{BN}} + E_0 x + E_1 x^2] (1-x) + [E_2 + E_3 x] x^2 (1-x)^2. \quad (3)$$

Here,  $E_g^{h\text{BN}}$  is the energy gap of undoped  $h$ -BN,  $E_0$  is the optical bowing parameter,  $E_1, E_2, E_3$  are the higher order corrections to the bowing parameter, obtained by the fitting procedure given in Table 1. We observe that the concentration dependence of the band gap results of Bernardi *et al* [25] performed for larger zigzag interface unit-cell, fit nicely with the form given in Eq (1) shown in Fig 3(b).

### (b) Formation energy and phase stability

The formation energy  $\Delta E_B$  Fig. 3(c) was calculated using the equation,

$$\Delta E_B = E\{C_x(\text{BN})_{1-x}, a(x)\} - [xE(C, a_C) + (1-x)E(h\text{BN}, a_{h\text{BN}})], \quad (4)$$

where  $E\{C_x(\text{BN})_{1-x}, a(x)\}$  is the total energy per atom of  $C_x(\text{BN})_{1-x}$  at the equilibrium in-plane lattice constant  $a(x)$ ;  $E(C, a_C)$  and  $E(h\text{BN}, a_{h\text{BN}})$  are the total energies per atom of undoped Graphene and  $h$ -BN at the equilibrium in-plane lattice constants  $a_C$  and  $a_{h\text{BN}}$ , respectively.

From the calculated formation energy, we investigated the phase stability [40, 41] of  $C_x(\text{BN})_{1-x}$  by fitting the calculated data with a parabola, expressing  $\Delta E_B(x) = 4\Delta H x(1-x)$ , where  $\Delta H$  is the formation energy at  $x = 0.5$ . In the regular solution model, the entropy of mixing can be expressed as

point probabilities or the concentration  $x$  as,  $S = -k_B[x \ln x + (1-x) \ln(1-x)]$ , where  $k_B$  is the Boltzmann constant. The Free energy is expressed as  $F(T, x) = \Delta E_B(x) - TS$ . At low temperatures  $F(T, x)$  shows a maximum at  $x = 0.5$ , and two minima located symmetrically away from  $x = 0.5$ . With increasing temperature these two minima converge to give rise to a single minimum at a critical temperature  $T_C$  at  $x = 0.5$ . The critical temperature was obtained from the equation, fulfilling the condition that  $d^2F/dx^2 < 0$  is unstable and bounded by the spinodal line, given by [40],

$$k_B T = 8 \Delta H x(1-x). \quad (5)$$

Thus, the critical temperature,  $T_C = 2\Delta H/k_B$ , was estimated to be 3850K for the zigzag and 6090K for the armchair interfaces, respectively. Therefore it is expected  $C_x(\text{BN})_{1-x}$  would be in the disordered phase above those temperatures. A lower bound of  $T_C$  can be obtained by estimating  $\Delta H$  directly from interpolation of the calculated  $\Delta E_B$  at  $x = 0.5$ , yielding the transition temperatures to be 3390K and 5060K for the zigzag and armchair interfaces, respectively.

We have also investigated the phase stability of  $C_x(\text{BN})_{1-x}$  by using the fit  $\Delta E_B(x) = H_0 + H_1 x(1-x) + H_2 x^2(1-x)^2$ , which gives better than parabolic fit shown in Fig 3(c) as full lines. Inclusion of such higher order terms in  $\Delta E_B(x)$  leads the transition from binodal to spinodal line to occur at temperatures lower than in the previous model. The free energy was calculated numerically and the  $T_C$  was found to be 4869K for the armchair and 3389K for the zigzag interface [38], respectively. We would like to mention that above calculations for larger supercells are under investigation and will be reported later.

The in-plane lattice constant of  $C_x(\text{BN})_{1-x}$ ,  $a(x)$  shows a deviation from Vegard's law [42] in Fig. 3(d), which has been fitted to,

$$a(x) = x a_C + (1-x) a_{h\text{BN}} + A x(1-x). \quad (6)$$

Here,  $A$  is the deviation parameter for the lattice constant  $a$ , obtained from fitting. The fitting parameters in Eqs. (1), (3) and (4) are given in Table 1.

Table 1: Numerical value of the parameters in Eqs (3), (5) and (6).  $E_0, E_1, E_2, E_3$  are in eV,  $\Delta H$  in eV/atom and  $A$  in Å, respectively. The values of  $E_n$  without parenthesis refer to that of the band gap at K-point and those within parenthesis to the indirect band gap, respectively.

Interface	$E_0$	$E_1$	$E_2$	$E_3$	$\Delta H$	$A$
Armchair	-5.0 (0.1813)	-3.993 (-10.823)	-48.698 (-76.328)	116.768 (158.151)	0.262	0.028
Zigzag	-16.554 (-17.952)	18.333 (25.333)	11.053 (23.568)	-6.605 (-52.396)	0.166	0.022

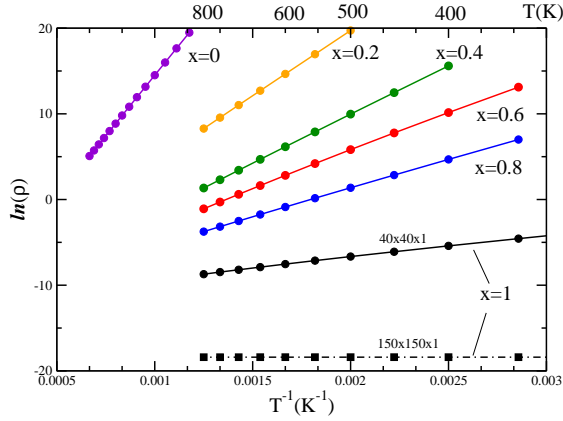


Figure 4:  $\ln(\rho(T))$  plotted against  $T^{-1}$  for  $C_x(\text{BN})_{1-x}$  at different concentrations calculated from the Boltzmann transport theory [28] at different concentration.

### (c) Resistivity from the Transport theory

Now we turn to our results of the resistivity  $\rho(T)$  of  $C_x(\text{BN})_{1-x}$  from the transport calculations. The resistivity of CBN nanomaterials was measured earlier [7, 18]. It was reported that  $\ln(\rho)$  varies linearly with  $T^{-1}$  for different concentration of B and N, indicating that CBN is semiconducting. The band gap  $E_g$  of CBN was estimated from Eq. (7) [27]. In Fig. (4) we show the results of  $\ln(\rho)$  against  $T^{-1}$ , assuming  $\tau = 10^{-14}$  s, for the zigzag interface of  $C_x(\text{BN})_{1-x}$  at  $x = 0, 0.2, 0.4, 0.6, 0.8, 1$ , in the temperature range of 200K to 800K. The calculated data can be fitted very well to straight lines as shown in Fig 4 and the band gap  $E_g$  at each concen-

tration was calculated from the slope of the lines using the relation,

$$\rho(T) = \rho_\infty \exp(E_g/2k_B T). \quad (7)$$

As mentioned earlier the k-point mesh had to be enhanced to  $150 \times 150 \times 1$  for pure Graphene ( $x = 1$ ) to capture the Dirac-point correctly. Also, for the pure  $h$ -BN we had to calculate  $\rho(T)$  at higher temperatures to obtain the measurable slope as shown in Fig. 4. In Table 2, the band gap  $E_g$  of  $C_x(\text{BN})_{1-x}$  calculated from the transport theory and those calculated directly using DFT are compared. We find an overall good agreement. It should be mentioned that the numerical value of the relaxation time  $\tau$  does not affect the the band gap estimation from the slope of Fig 4, since the constant  $\rho_\infty$  in Eq (7) will only shift the origin of the lines in Fig 4 and not affect their slopes. Any discrepancy of the calculated  $E_g$  should thus come from inadequate k-point mesh. To our knowledge, this is apparently the first calculation of  $\rho(T)$  for the semiconducting nanomaterial  $C_x(\text{BN})_{1-x}$  from Boltzmann transport theory.

### (d) Charge density and the PDOS

Finally, in Fig. 5 we show the PDOS and the valence charge density on all in-equivalent atoms across the armchair (Figs. 4a and 4b) and the zigzag (Figs 4c and 4d) interfaces of  $C_x(\text{BN})_{1-x}$  at  $x = 0.6$ . The calculated PDOS give a idea about the contributions coming from each in-equivalent C, B and N atoms towards the total DOS shown in Fig. 2. The

Table 2: Band gap calculated by Bandstructure and Boltzmann transport theory for  $C_x(\text{BN})_{1-x}$  for zigzag interface at different concentrations.

$x$	Bandstructure (Quantum Espresso)	Using Eq. (7) and Fig. (4) (Boltztrap)
0	4.557	4.87
0.2	1.919	2.63
0.4	1.008	1.97
0.6	0.709	1.53
0.8	0.812	1.153

calculated valence charge density (Figs 4b and 4d) indicates that covalent *sp*-bonding nature is preserved in  $C_x(\text{BN})_{1-x}$ .

The band structure and the DOS of  $C_x(\text{BN})_{1-x}$  are somewhat different for the zigzag interface than armchair interface. The bands immediately above and below the energy gap are more flat, as evidenced by a strong peaks in the DOS. It should be noted that unlike in the armchair interface, in zigzag interface the C atoms are terminated by either all B-atoms or by all N-atoms (Fig. 1). This leads to different type of excess charge at the interfacial C-atoms. We have calculated this excess charge from the difference of the Löwdin charges between the similar atoms in  $C_x(\text{BN})_{1-x}$  and that of undoped Graphene and *h*-BN [38].

We found, a C-atom terminated by a B (N) atom at the zigzag interface would have more negative (positive) charge than that in undoped Graphene; whereas on the zigzag interface on the other side of the same domain the excess charge on the interfacial C atom would be reversed. This leads to strong peaks in the DOS above or below  $E_F$ , which alternates as one goes onto atoms lying deeper in the domain. This effect is illustrated in Fig. 4c where we show the calculated PDOS on C-atoms going from one end of the zigzag interface to the other end. Comparing the excess charges on the interfacial C atoms, for both armchair and zigzag interfaces, we found higher is this excess charge, larger is the band gap  $E_g$ .

Present calculations may be extended to include higher order corrections to the exchange-correlation energy using HSE [43] or GW [44] methods to check the validity of our results. However, the GGA exchange-correlation kernel used in present calculations yields the groundstate physical properties of Graphene and *h*-BN, in good agreement with experimental results.

In conclusion, we have presented a detail first-principles calculation of the band structure, DOS, the band gap and the formation energy of  $C_x(\text{BN})_{1-x}$  at different concentrations. From the formation energy, we have also investigated the phase stability of the material using a regular solution model. Although we have used only the single-site probabilities for

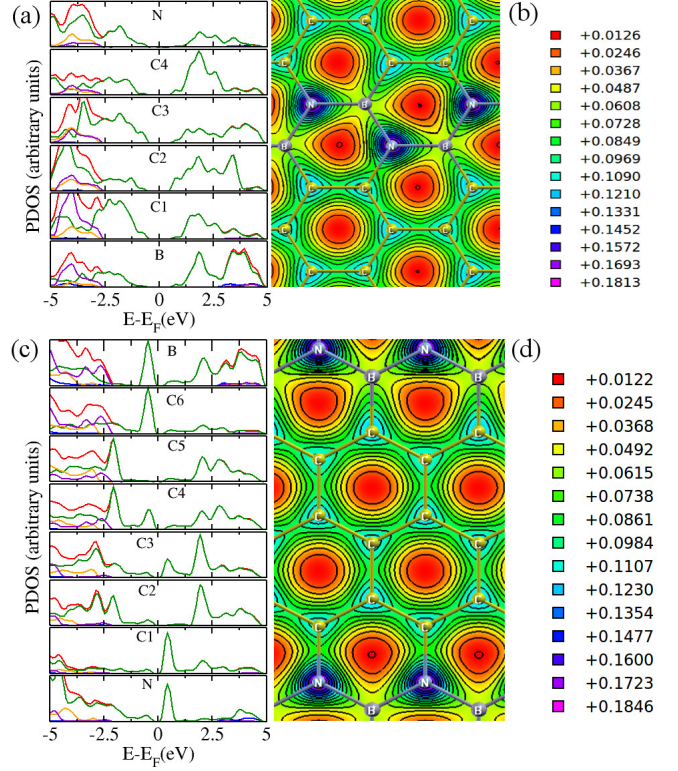


Figure 5: (a) : Calculated PDOS on the in-equivalent B, C and N atoms in the unit-cell. C1, C2, C3, C4 denote four C-atoms on the upper hexagon, terminated by B and N shown in (b). The PDOS referring to  $2s$ ,  $2p_{\text{total}}$ ,  $2p_z$ ,  $2p_x$  and  $2p_y$  orbitals are shown in blue, red, green, orange and violet, respectively. (b) : Calculated valence charge density shown across the armchair interface between Graphene and *h*-BN domains. The contours are in the units of  $e/\text{Bohr}^3$ . (c) : Calculated PDOS on the in-equivalent B, C and N atoms in the unit-cell. C1 ... C6 denote six C-atoms on the chain, terminated by N and B atoms on two opposite zigzag interfaces shown in (d). (d) : Calculated valence charge density shown across the zigzag interface between Graphene and *h*-BN domains. (a) and (b) refer to  $C_{0.6}(\text{BN})_{0.4}$  armchair interface, whereas (c) and (d) refer to the zigzag interface.



the entropy, which can be improved further by incorporating the pair or cluster probabilities, we have given an estimate of the transition temperature for the order-disorder transition in  $C_x(\text{BN})_{1-x}$ , apparently for the first time. We have calculated the resistivity of  $C_x(\text{BN})_{1-x}$  using Boltzmann transport theory and have estimated the band gap of this semiconducting nanomaterial at different concentrations which agrees with earlier experimental observations. Our calculated DOS and PDOS should motivate further angle resolved photoemission spectroscopic (ARPES) measurements on this technologically important nanomaterial.

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